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Screening Polynuclear Aromatic Pollutants in Ambient and Indoor Air by Synchronous Luminescence*

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INTRODUCTION

The characterization of polynuclear aromatic (PNA) compounds in ambient and indoor environments is of great importance because many of these compounds are known to be converted by metabolic activation to ultimate carcinogens[1] and could pose serious potential human health hazards. Health assessment studies of the exposure of any given population group to PNA pollutants could be costly because these studies require extensive and long-term monitoring and analysis programs involving large numbers of samples and the use of sophisticated analytical techniques, such as high-performance liquid chromatography (HPLC) and gas-chromatography/mass spectrometry (GC/MS). In many monitoring situations, the determination of all individual PNAs may be unnecessary and a screening phase to identify critical problem areas can reduce the cost of monitoring programs.

This paper discusses the results of a field study designed to evaluate a screening procedure based on synchronous luminescence (SL), for ranking air samples according to their total PNA content[2,3]. The SL technique can be used not only for chemical detection, but also for monitoring biological markers, such as carcinogen-DNA adducts in human biological fluids due to exposure to PNA pollutants[4-6].

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This project was conducted by Oak Ridge National Laboratory (ORNL) in conjunction with a pilot sampling and analysis field study, which was was performed by Battelle's Columbus Laboratories (BCL)(7), involving eight residences and two background homes located in Columbus, Ohio. Air samples were collected on quartz fiber filters followed by polyurethane foam (PUF) cartridges. These air samples, collected by active medium-volume samplers, were extracted by BCL, analyzed by GC/MS and concurrently sent to ORNL for SL screening.

EXPERIMENTAL

Synchronous Luminescence Screening

The screening procedure evaluated in this field study is based on the synchronous luminescence (SL) technique. In conventional luminescence spectroscopy, only one of the two spectral wavelengths, λ_{em} (emission) or λ_{ex} (excitation), is scanned while the other remains fixed. For complex samples, the resulting spectra obtained with this conventional procedure are often poorly resolved and featureless because of spectral overlap between the emissions from individual components. However, by scanning both λ_{em} and λ_{ex} synchronously with a constant interval, $\Delta\lambda$, between the two wavelengths ($\lambda_{em} - \lambda_{ex} = \Delta\lambda$, usually 3-5 nm for PNAs), the luminescence spectrum becomes more resolved with sharp peaks that are more readily identified(8-10).

Analytical Protocol

The three major steps involved in the protocol are: (a) serial dilution of sample extracts, (b) SL measurement, and (c) ranking the samples.

Serial Dilution. Upon receipt, all air particulate sample extracts (in methylene chloride) were further diluted in ethanol without sample cleaning or fractionation. Three serial dilutions were made per sample.

SL Measurements. In this field study, the synchronous scanning technique greatly enhanced the resolution of fluorescence spectra and was used for fluorescence measurements. The diluted solutions of each sample were introduced into standard 1 x 1 cm quartz cells for synchronous fluorescence scanning. The SL profiles were recorded from 260 to 500 nm using $\Delta\lambda$ = 4 nm.

RESULTS AND DISCUSSION

The advantage of a screening technique, such as SL, is the ability to rank several samples with regard to relative PNA content with very little sample preparation and at a low cost. This can decrease the a number of detailed analyses by GC/MS or HPLC: selection can be made for analysis of those samples containing the highest levels of PNAs. It is also possible using SL to distinguish between relative amounts of PNA compounds having differing molecular weights.

Figure 1 shows examples representing three types of residences with different environmental conditions monitored in this study. Figures 1a, 1b, and 1c correspond to indoor air samples (8-hour, PUF + Filter extracts) of a gas-heated home with smokers, a gas-heated home with a fireplace, and a home with only electric heaters. A rapid examination of the intensity distribution of the three SL profiles

qualitatively provides several conclusions. As a general rule, the larger the number of rings an aromatic compound contains, the longer the wavelength at which its emission band occurs(8). An SL band below 300 nm region indicates the presence of a monocyclic species, whereas, an SL band in the 300 to 380 nm regions reveals the presence of compounds containing two or three benzene rings. An SL band above 380 nm shows the presence of compounds containing four or more benzene rings. For example, in Figure 1a, the weak SL peaks at 286 and 308 nm are indicative of monocyclic compounds in the house with smokers. The SL band at about 330 nm is representative of compounds with two benzene rings. The clusters of overlapping peaks from 350 to 500 nm spectral region reflect the abundant presence of PNA species with three to seven benzene rings. The houses with fireplaces and electric appliances (Figures 1b and 1c) exhibit different SL spectral structures with intense peaks at 286 and 308 nm. The SL peak at 390 nm is due to the spiked reference compound, 9-phenylanthracene, added to the sample as the internal standard for quantitative GC/MS analyses.

Figure 2 shows an example of comparative results of the SL emission peak at 362 nm for homes with smokers vs. homes without smokers. These results indicate a significantly higher PNA content due to the presence of cigarette smokers in the home. The higher PNA levels due to smoking activities and reflected in the overall SL ranking were found in all indoor sampling locations. Outdoor samples show lower PNA content than indoor samples. Detailed discussion of the effects of other factors, including gas appliances, fireplaces, electric heaters, is presented elsewhere(11).

The air sample extracts screened by SL have been independently analyzed by Battelle Laboratories using GC/MS. The GC/MS analysis provided the content of fifteen PNA compounds, including quinoline, isoquinoline, phenanthrene, anthracene, fluoranthene, cyclopenta(c,d)pyrene, benzo(a)anthracene, chrysene, benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, and coronene7. The total SL ranking indices were computed by summing all the normalized SL peaks at 286, 308, 330, 362, 390, 408, 440, and 480 nm, and the results compared with the total concentrations of the fifteen PNAs. A ranking index to characterized PNA in environmental samples has been described3. The correlation coefficient for the comparison between the SL ranking data and the GC/MS results is 0.72. Examples of comparative results between the SL ranking indices and the GC/MS data are illustrated in Figure 3. Considering the simplicity and rapidity of the SL procedure, this correlation is considered quite satisfactory for a screening phase.

The results obtained in this study demonstrate the sensitivity and usefulness of the SL screening procedure for monitoring indoor air pollution. The concentrations of PNAs detected using GC/MS are in good agreement with the results predicted by the SL screening measurements. Although the usefulness of analytical techniques such as GC/MS and HPLC is well established for detailed characterization of individual compounds, it is not cost-effective to apply these tools systematically to all samples, especially when many of the samples contain low levels of PNAs or similar PNA constituents that can be predicted in a screening phase. Before selection of which group of samples is to be analyzed in detail or which analytical technique is to be utilized, it is desirable to have some screening procedure to prioritize samples. Such a screening step may obviate the need to perform unnecessary and costly detailed analyses and will lower the cost of health effect assessment studies.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Figure 1: Examples of SL Spectral Profiles of Indoor Air Sample Extracts.

a) Gas heated home with smokers (sample E_b)
b) Gas heated home with fireplace (sample A_1)
c) Electric heated home (sample G_b)

Figure 2: Effect of Cigarette Smoking on the SL Emission Peak at 362 nm.

Figure 3: Examples of comparative results of SL ranking indices and GC/MS data for 15 PNA pollutants (see text).

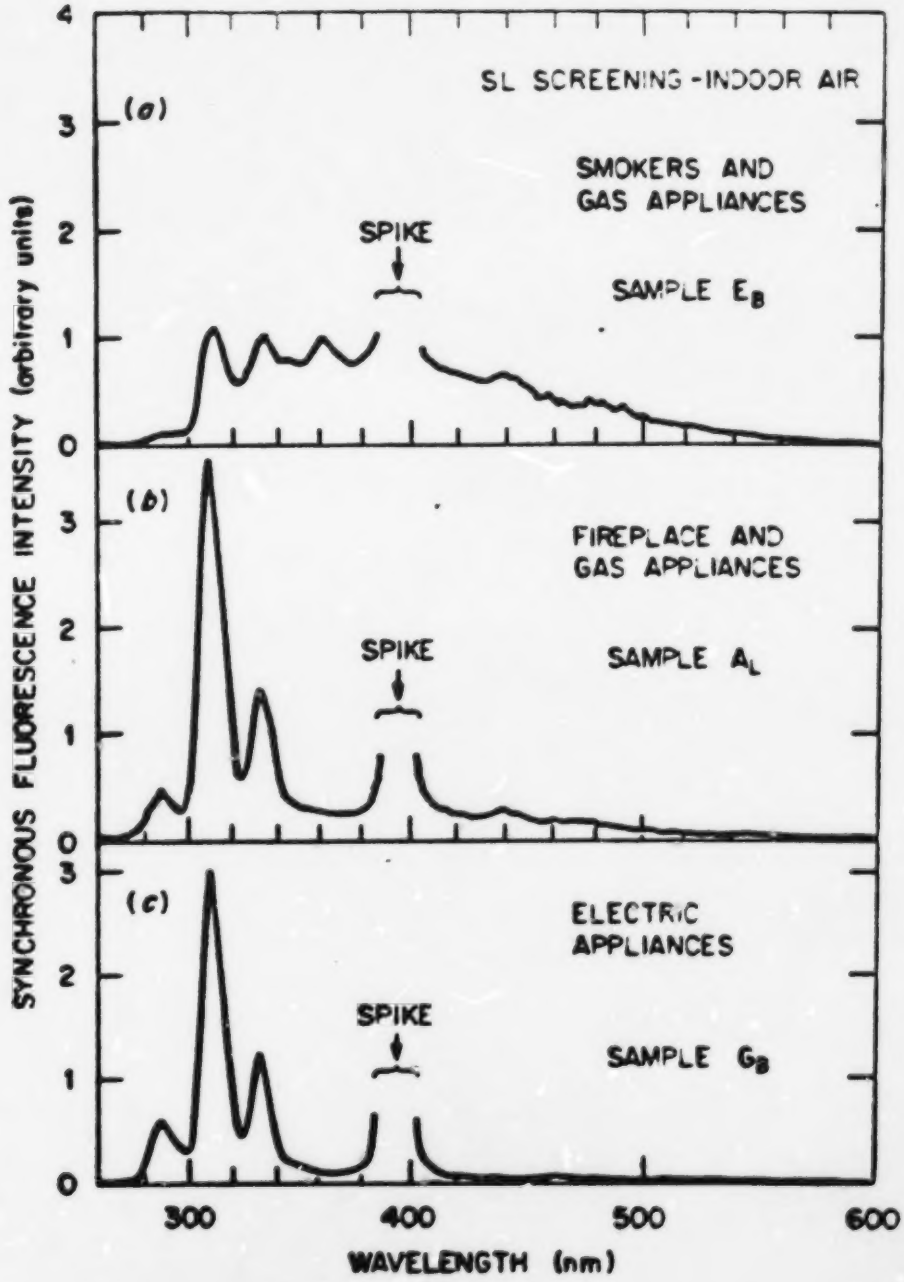
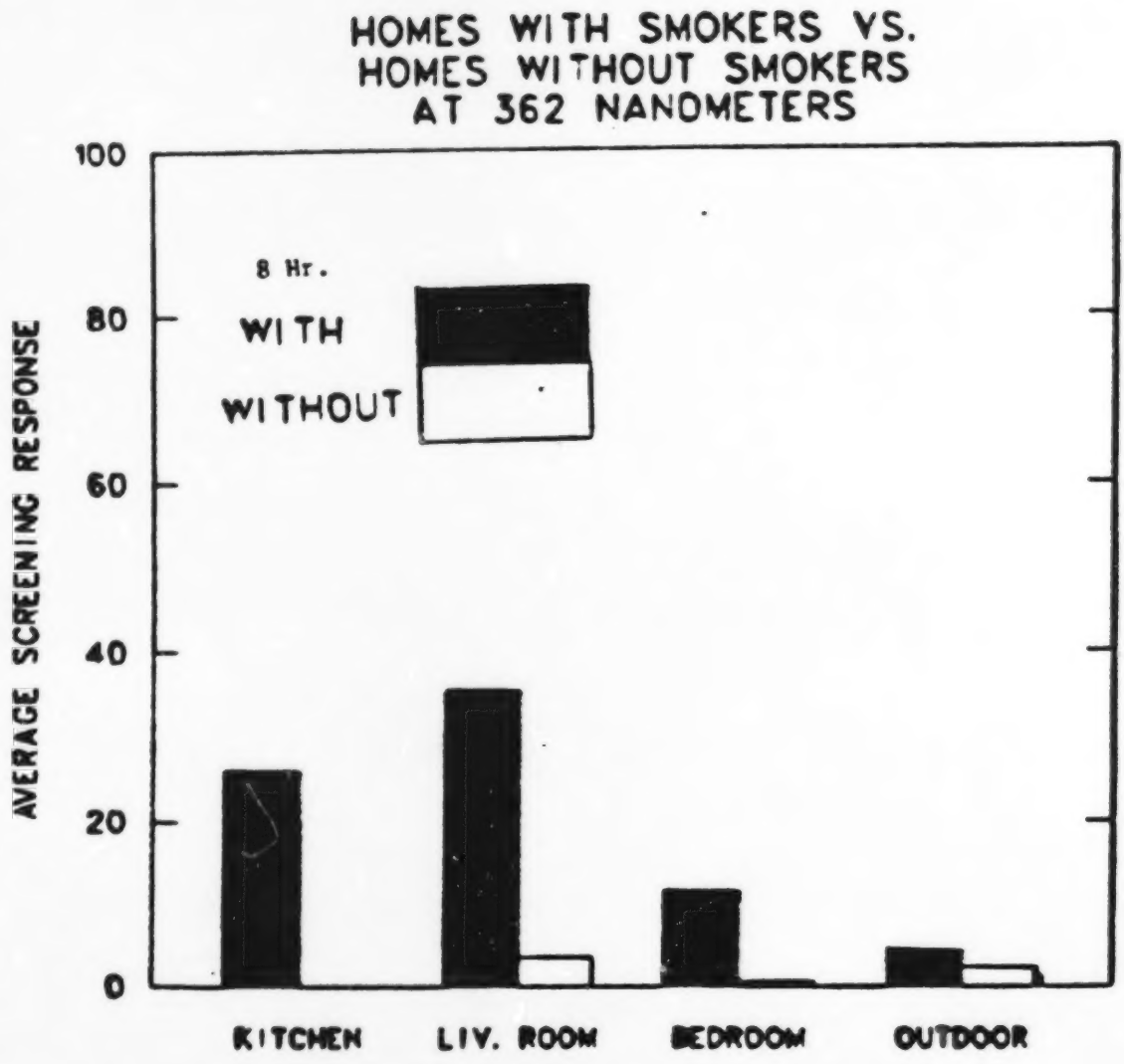


Figure 1: Examples of SL Spectral Profiles of Indoor Air Sample Extracts.

a) Gas heated home with smokers (sample E_b)
b) Gas heated home with fireplace (sample A_l)
c) Electric heated home (sample G_b)



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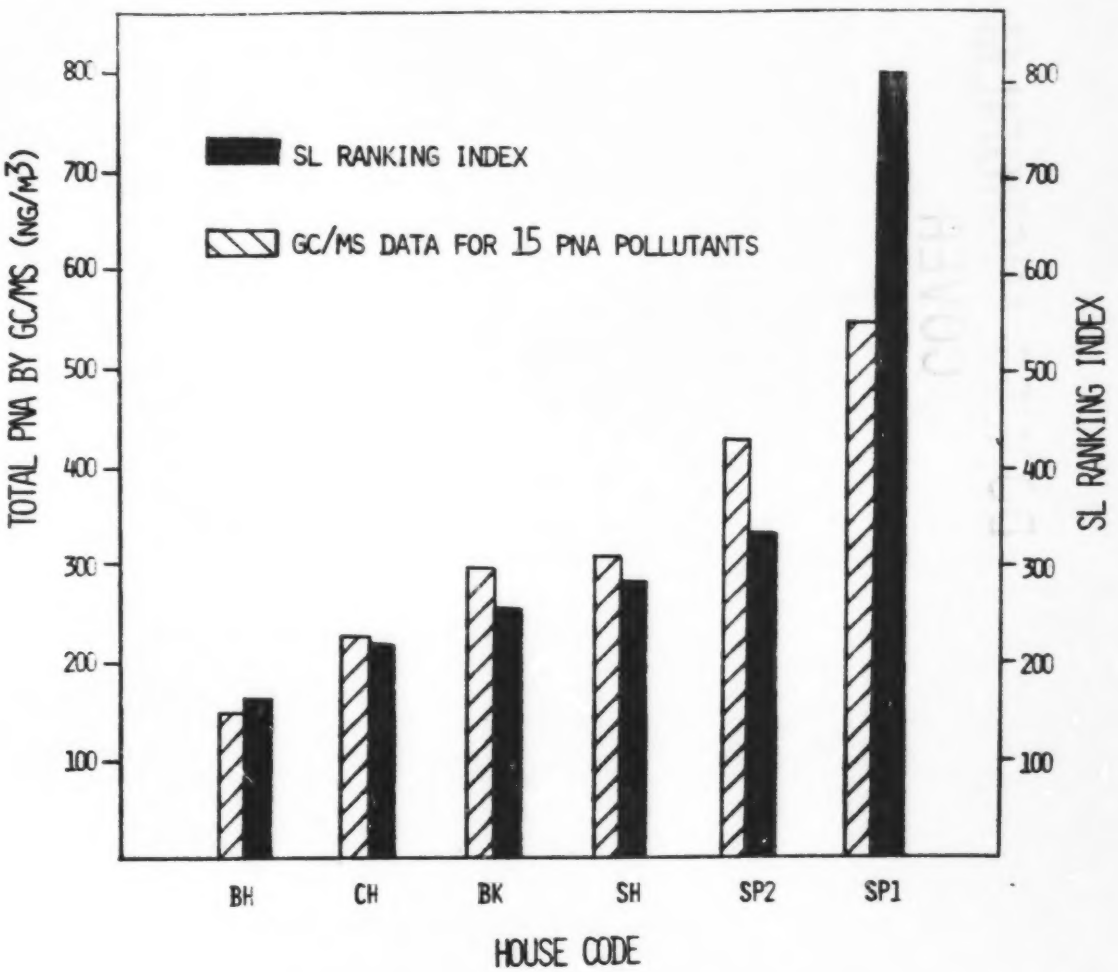

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